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14. ABSTRACT

Kapton® is ubiquitous in space-structures, yet degrades severely in low Earth orbit (LEO) due to reactions with atomic oxygen (AO). Polyhedral oligomeric silsesquioxane (POSS) is a cage-like structure of silicon and oxygen, surrounded by organic groups. Both main-chain (MC) and side-chain (SC) POSS-diamines have been polymerized to form POSS-Kapton®-polyimides (POSS-Kapton®-PIs) which have comparable resistance to AO. POSS-copolymers form an AO-resistant silica layer upon exposure to AO, which has been identified by X-Ray Photoelectron Spectroscopy (XPS). Images of space-flown MC-POSS-Kapton®-PIs, physical properties of both MC-POSS-Kaptons® and SC-POSS-Kaptons®, and transmission electron micrographs of MC-POSS-Kaptons® will be presented.

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The Effect of Atomic Oxygen on POSS-Polyimides
(Preprint)

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Kapton® is ubiquitous in space-structures, yet degrades severely in low Earth orbit (LEO) due to reactions with atomic oxygen (AO). Polyhedral oligomeric silsesquioxane (POSS) is a cage-like structure of silicon and oxygen, surrounded by organic groups. Both main-chain (MC) and side-chain (SC) POSS-diamines have been polymerized to form POSS-Kapton®-polyimides (POSS-Kapton®-PIs) which have comparable resistance to AO. POSS-copolymers form an AO-resistant silica layer upon exposure to AO, which has been identified by X-Ray Photoelectron Spectroscopy (XPS). Images of space-flown MC-POSS-Kapton®-PIs, physical properties of both MC-POSS-Kaptons® and SC-POSS-Kaptons®, and transmission electron micrographs of MC-POSS-Kaptons® will be presented.

Introduction

Polyimides consist of stiff aromatic backbones and belong to a class of polymers that are called polyheterocyclics. They are known for their thermal stability, chemical solvent resistance, mechanical properties, and reasonable cost. Polyimide synthesis and processing was pioneered by workers at Dupont in the 1950's with Kapton® being the first commercially significant polyimide. Polyimides are generally formed in a polar solvent through the condensation of a dianhydride monomer and a diamine monomer. High molecular weight poly(amic acid) readily forms by the nucleophilic attack of an amino group on an anhydride carbonyl group. The poly(amic acid) then undergoes either chemical imidization, or solvent evaporation followed by thermal imidization. During imidization the poly(amic acid) forms polyimide through ring-closure and concurrent loss of water.[1,2]

Many studies have been carried out on the structure-property relationships of polyimides. It has been found that subtle variations in the structures of the dianhydride and diamine components have large effects on the properties of the final polyimide. An example is the overall flexibility of the polyimide chain, as seen through parameters such as the glass transition temperature (T_g), which decreases substantially with increasing asymmetry and flexibility in the polyimide backbone.[1]

Kapton® is used in electronics, commonly as an interlayer dielectric material in microelectronics, due to its low dielectric constant of about 3.4 (measured at 1 Hz). This feature of Kapton® helps to prevent cross-talk between conducting wires. Kapton® has also been widely used as aircraft wire insulation in the automotive industry. Kapton® is ubiquitous in space applications due to its temperature stability, insulation properties, IR transparency, low solar absorptance, resistance to UV damage, and excellent optical properties.[3]

Despite the desirable properties of Kapton®, all organic polymeric materials severely degrade in low Earth orbit due to reactions involving atomic oxygen (AO), which can be up to 90% of the atmosphere at altitudes of 500 km. Traditionally, Kapton® is protected by the application of a silica coating (approximately 0.13 microns thick) since it imparts resistance to degradation in the presence of AO. However, imperfections in the silica layer created during it's deposition, or by physical damage that occurs during flight, lead to Kapton® erosion.[4-21] For this reason, alternative and self-regenerative methods of protection are sought for organic polymeric materials used in space applications.

Our focus has been on the incorporation of POSS into Kapton® through copolymerization of POSS-diamine monomers.[22-29] POSS is a unique family of nanoscale inorganic/organic hybrid cage-like structures that contain a silicon/oxygen framework ($RSiO_{1.5}$), surrounded by alkyl or aryl groups that can be utilized as polymer compatiblizers or as polymerizable functional groups.[28] We have found with POSS-F6 polyimide ("clear polyimide") and POSS-Kapton®-polyimide that appropriate POSS-diamines can be incorporated into the poly(amic acid) polymerization without changes to polymerization conditions, or changes to the subsequent cure cycles.

Using simulated LEO environments, we have discovered that copolymerized MC-POSS and SC-POSS impart approximately the same amount of AO-resistance to Kapton® and other polyimides, regardless of POSS structure and distance from the polyimide backbone. 0 wt %, 1.75 wt%, and 3.5 wt % Si_8O_{11} MC-POSS-Kapton® samples flew in LEO on the International Space Station for 3.9 years. 0 wt % POSS-Kapton® completely eroded within 4 months, and a thin film of 3.5 wt % Si_8O_{11} MC-POSS- Kapton® survived the flight.[25]

In learning about the effect of POSS on the AO resistance and physical properties of POSS-Kaptons®, we may gain insight by considering how POSS is incorporated into the polymer and how it affects chain packing in the polymer matrix. The inherent strength and solvent resistance of Kapton® is derived from its strong intermolecular interaction between charge transfer complexes in adjacent polymer chains. These interactions would obviously be interrupted by the incorporation of a bulky molecule such as POSS. It is believed that the POSS-diamine is randomly copolymerized into the polyimide backbone due to the expected lower reactivity of POSS-diamines relative to the Kapton® diamine monomer, oxydianiline. This is deduced from studies of the effects of monomer structure on reactivity. It has been found that dianhydrides containing

bridging electron-withdrawing groups, such as a carbonyl, are more reactive than those containing bridging electron donating groups such as an oxygen (O).[1] The trend also exists, yet with less consistency, that diamine monomers containing bridging electron donating groups (O) are more reactive than those containing a bridging electron withdrawing group, such as POSS. The effect of POSS on the polymer can be somewhat elucidated by transmission electron microscopy (TEM), energy dispersive X-ray analysis (EDX), and physical property characterization.

This work focuses on the physical properties of MC- and SC-POSS-Kaptons[®], the comparison of their AO-resistance in a simulated LEO environment, and the effects of Materials International Space Station Experiment (MISSE1 and MISSE5) flights in LEO on MC-POSS-Kapton[®]-polyimides.

Experimental

Synthesis of Side-Chain POSS Monomers

N-{3-($R_7Si_8O_{12}$)propyl}-3,5-diaminobenzamide [R = *iso*-butyl & cyclohexyl] were synthesized from 3-aminopropyl-hepta(alkyl)POSS (where alkyl is *iso*-propyl or cyclohexyl) in excess of 95 % yield. The synthesis of SC-POSS has been described in detail.[30]

Synthesis of POSS-Polyimide Copolymers

Due to the ease of separation of catalyst from product, N-{3-(*iso*-butyl$_7Si_8O_{12}$)propyl}-3,5-diaminobenzamide was used for the copolymerization with the Kapton[®] monomers 4,4´-oxydianiline (ODA) and pyromellitic dianhydride (PMDA) in N,N´-dimethylacetamide (DMAc) solvent. [25, 30]

Low Earth Orbit Exposure of POSS-Polyimides

MC-POSS-Kaptons[®] containing 0, 1.75, and 3.5 wt % Si_8O_{11}, were cast and cured onto aluminium substrates and flown in LEO on the outside of the International Space Station as part of the MISSE1. The flight experiment was launched on August 10, 2001 and was retrieved after 3.9 years. The samples were exposed to the RAM and therefore all aspects of the LEO environment including AO and UV light. The step-height difference between the unexposed sample area and the neighbouring exposed sample area was measured in twelve locations using profilometry. The atomic composition of sample surfaces was determined by XPS.[25]

Free standing films of MC-POSS-Kaptons[®] containing 0, 1.75, 3.5, 5.25, and 7.0 wt % Si_8O_{11} were sewn to a Kapton[®] blanket and flown in LEO on MISSE5 for about one year. The AO fluence was estimated at 1.8 x 10^{20} atoms cm^{-2}, based on the Kapton[®] recession rate during this flight.

Exposure of POSS-Kapton[®]-Polyimides to Atomic Oxygen

Ground-based AO exposures of POSS-PI samples were performed with a pulsed AO

beam, operating at a repetition rate of 2 Hz and containing O-atoms that were generated by the laser-induced breakdown of O_2 gas in a conical nozzle with the use of a 7-joule-per-pulse CO_2 laser [23-28]. The hyperthermal beam contains neutral O-atoms and molecular oxygen, with an ionic component of 0.01%. The mole fraction of AO in the beam was above 70 % and, for some exposures, above 90 %. Kinetic energies of the fast O-atoms in the beam can range from 2 to 15 eV, with the average being about 5.2 eV. Prior to exposure, samples were covered with a stainless steel mesh disk in order to mask areas and achieve both AO exposed and unexposed areas. The O-atom fluence was on the order of 10^{20} O-atoms/cm^2 for all experiments. All samples were handled in ambient air after exposure and prior to etch depth determination by profilometry, surface topography, and surface chemistry measurements.[27]

Surface Characterization of POSS- Kapton®-Polyimide Films

XPS data was obtained with the use of non-monochromatized Mg Kα radiation (1253.6 eV) and a hemispherical CLAM 2 (VG Microtech) analyzer. Scanning electron microscopy (SEM) was performed using an ISI CL6 operating at 15 keV equipped with a Kevex X-ray detector, at Edwards AFB, as previously reported. [25, 29] SEM images of MISSE1-flown samples were acquired similarly, at Montana SU.

TEM images were obtained on either a Hitachi H7600 transmission electron microscope at 120 kV or a Hitachi HD2000 STEM at Clemson University Electron Microscope Facility, SC.

Physical Property Characterization of POSS- Kapton®-Polyimides.

Polyimide samples were analyzed using a DMTA V from TA Instruments with a 5 ºC/min temperature ramp from room temperature to 500 ºC in tensile mode.[18] Measurements of the coefficient of thermal expansion (CTE) were taken on a thermo-mechanical analyzer (TMA 2940) from TA Instruments with a film fiber attachment in a nitrogen atmosphere. The cured films were cut into 15mm by 3mm samples, the force applied was 0.05N & 0.10 N, and the sample was heated at 5 °C/min. The CTE was calculated as $\alpha = (\Delta L \times K)/(L \times \Delta T)$ where L = length, K = a cell constant, T = temperature in °C. Test variability was +/- 2.306 ppm/ ºC based on five Kapton H® tests.

Results and Discussion

Two side chain (SC) POSS-diamines were synthesized in nearly quantitative yield (>95%) from a POSS starting material that is commercially available and economical on a large scale. 3-Aminopropyl-hepta(alkyl)POSS (where alkyl is *iso*-propyl or cyclohexyl) was used to produce diamines N-{3-($R_7Si_8O_{12}$)propyl}-3,5-diaminobenzamide [R= *iso*-butyl & cyclohexyl].[30] The SC-POSS-diamine N-{3-(*iso*-butyl$_7Si_8O_{12}$)propyl}-3,5-diaminobenzamide was more easily separated from the reaction catalyst and used for all polymerizations with polyimide monomers in this work. MC-POSS-diamine and SC-POSS-diamine were separately copolymerized with the Kapton® monomers without changes to the Kapton® polymerization procedure, resulting in the POSS-Kaptons® shown

in Figures 1 and 2. Approximately the same weight % POSS cage was used for both MC-POSS and SC-POSS containing polymers. The amounts were inherently approximate because MC-POSS is a Si_8O_{11} structure, while SC-POSS is a Si_8O_{12} structure. It should be noted that 3.5 and 7 wt % POSS cage equal about 10 and 20 wt % MC-POSS-diamine monomer (as reported in previous publications) [11, 22, 25, 27-30], and 8.5 and 17 wt % SC-POSS-diamine monomer respectively, in the POSS polyimides.[30] This means that less SC-POSS monomer may be used, relative to MC-POSS, to deliver the equivalent amount of POSS cage into the polymer matrix.
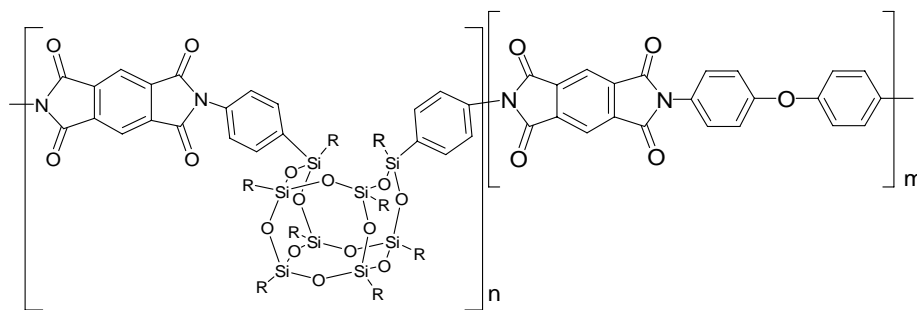
Figure 1. MC-POSS-Kapton® structure demonstrating the PMDA-MC-POSS repeat unit and the PMDA-ODA repeat unit, R = cyclopentyl.
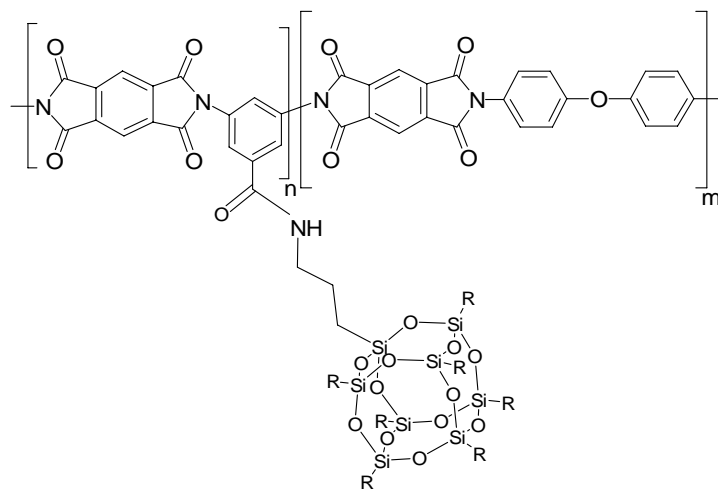

Figure 2. SC-POSS-Kapton® structure demonstrating the PMDA-SC-POSS repeat unit and the PMDA-ODA repeat unit, R = *iso*-butyl.

Visually comparisons of MC-POSS-Kapton® to SC-POSS-Kapton®, show that higher weight percents of SC-POSS were copolymerized before the films showed opaque regions. Visible white aggregates formed in the 10.5 wt % Si_8O_{11} MC-POSS-Kapton®, which was completely opaque and shattered during cure. On the other hand, 10.5 wt% Si_8O_{12} SC-POSS Kapton® is transparent with areas containing visible opaque streaks. 12.3 wt % and 14 wt % Si_8O_{12} SC-POSS-Kapton® have increasing brittleness and areas

of opaque streaks, but also have transparent flexible areas that mimic the amber color and appearance of Kapton[®]. This implies that fine tuning of processing parameters may lead to transparent and flexible films with higher SC-POSS loadings than achieved with MC-POSS.[31] Thus far, SC-POSS has been synthesized on the 50 gram scale and a 50 micron thick, 45 inch diameter film of 7 wt % Si_8O_{12} SC-POSS-Kapton[®] has been industrially produced (Figure 3).
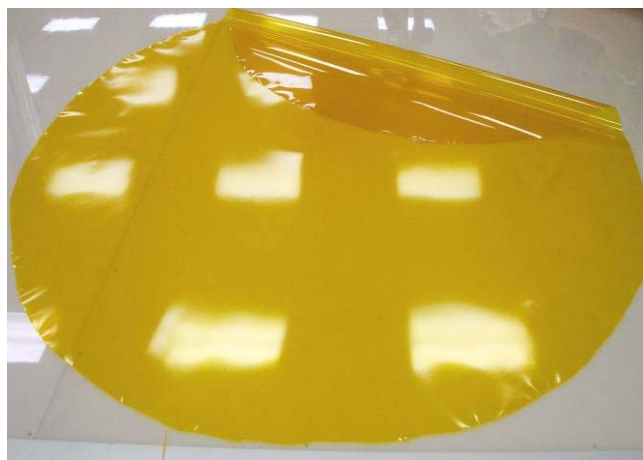

Figure 3. 45 inch diameter film of 7 wt % Si_8O_{12} SC-POSS-Kapton[®] (Photo courtesy of ManTech SRS Technologies Inc., Huntsville AL).

The addition of POSS had negligible effects on the coefficient of thermal expansion of POSS-Kapton[®] relative to 0 % POSS-Kapton[®]. In previous work [29, 30] it was shown that commercial Kapton H[®], 0 % POSS-Kapton[®], 7 wt % Si_8O_{12} SC-POSS-Kapton[®], 7 wt % Si_8O_{12} SC-POSS-Kapton[®] exposed to 2.3×10^{20} oxygen atoms cm^{-2}, and 7 wt % Si_8O_{11} MC-POSS-Kapton[®] have CTE values of 30.25, 33.11, 35.86, 33.64, and 33.5 ppm/ºC (test variability = ± 2.306 ppm/ºC). The measurements on the unexposed and AO-exposed SC-POSS Kaptons[®] were taken on different batches of material, which may have had slight variations in molecular weight and cure profile. The CTE of silica is < 1 ppm/ºC which is in mismatch with the CTE of Kapton[®] and contributes to the loss of the silica layer when enduring quick temperature changes and other conditions in LEO. We have shown through a detailed examination of AO-exposed, scratched, and re-exposed 8.75 wt % MC-POSS-Kapton[®] that the damaged silica layer is replenished in the presence of AO with a maximum loss of 200 nm of the POSS-Kapton[®] surface. [23, 25, 29]

The physical properties of SC-POSS-Kaptons[®] were evaluated by DMTA as shown in Figure 4. As the weight percent of SC-POSS cage content increased as follows: 0, 1.75, 3.5, 7, and 8.8, the glass transition temperature decreased as follows: 407 ºC, 403 ºC, 406 ºC, 392 ºC, and 365 ºC, respectively. The glass transition in polymers is generally accepted to represent the interrupted approach to a hypothetical thermodynamic state of zero configurational entropy. This state is not reached as the molecular motion that would allow close ordered packing decreases exponentially with decreasing temperature.[28,32, 33] Polymer chemical structure has a profound effect on T_g, in which chain flexibility, polarity, and pendent groups can increase or decrease the T_g.

When POSS is incorporated into the side chain of a polymer, both POSS-POSS and POSS-polymer interactions are expected. In POSS containing polymers, it has been shown that the large (1.5 nm) POSS monomer increases free volume and inter-chain spacing, as well as introducing a steric barrier that inhibits torsional rotation about the polymer backbone. Interestingly, there is a non-linear decrease in the T_g with increasing POSS loading, implying that the POSS addition is not exclusively a free volume effect, but also a function of POSS-POSS aggregation and POSS-polymer interactions. The POSS-matrix interactions disrupt the charge transfer complex of the polyimide, impeding imidization and affecting chain mobility. The broadening of the left hand side of the tan delta peak supports POSS group aggregation and phase separation, which is represented by the development of a beta transition. While a steric barrier to torsional rotation usually increases T_g, competing interactions of free volume and POSS aggregation, as well as disruption of the imidization reaction due to POSS incorporation, contribute to T_g depression.

Physical properties of MC-POSS-Kaptons® were evaluated by DMTA and have been discussed previously.[23, 25]   All T_g values, except for 8.8 wt % MC-POSS Kapton®, were slightly lower than those for the equivalent SC-POSS-Kaptons®. The tan δ plots were symmetrical, and the T_gs were as follows: 420 ºC for 0 % POSS-Kapton®, 394 ºC for 3.5 % Si_8O_{11} MC-POSS-Kapton®, 390 ºC for 7 % Si_8O_{11} MC-POSS-Kapton®, 383 ºC for 8.75 % Si_8O_{11} MC-POSS-Kapton®.

To better understand the effect of POSS on imidization kinetics, a series of POSS-Kaptons® were subjected to an extended hold at 275 ˚C for 16 hours. The storage modulus and tan δ curves versus temperature are shown in Figure 5. The T_g increased for 7.0 and 8.8% SC-POSS-Kapton® after the extended cure period. While the storage modulus and tan δ curves for the Kapton® without POSS are unchanged. iso-Butyl POSS has been shown to decrease the T_g and increase entanglement density in tethered co-polymers because of the increased free volume created by the POSS. [28] Yet, Figure 5 represents the effect that POSS has on the imidization kinetics of the polyimide. As the amount of SC-POSS increases, the ability for a strong charge complex between carbonyls and nitrogen groups are diminished. At an extended cure hold, further imidization occurs. This is demonstrated by the increase in T_g, as the bulk polymer mobility is decreased.

Further insight into POSS dispersion and POSS-POSS aggregation may be seen by TEM imaging of POSS-Kapton® films. Wei et al. carried out TEM imaging on POSS-end-capped Kapton® films, which were directionally blade-cast before cure. It was reported that POSS-POSS aggregates formed lamellae about 2-3 nm wide, as seen by layers of dark lines perpendicular to the film plane and casting direction, as well as by dark dots when the image was taken parallel to the film plane and casting direction. Interestingly, the Si-Si distance in a POSS cage is 0.5 nm and the width of a POSS cage with cyclohexyl groups is 1.5 nm.
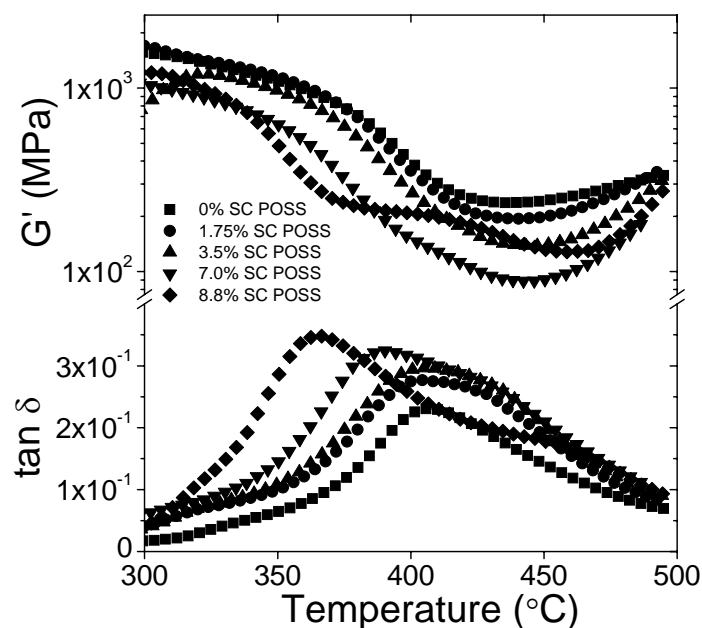
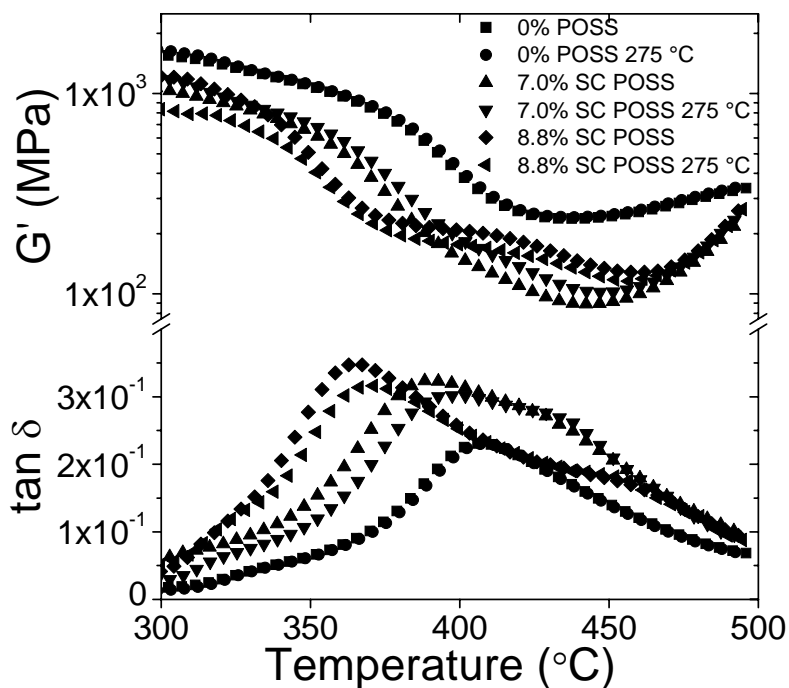Figure 4. Dynamic Mechanical Thermal Analysis of 0, 1.75, 3.5, 7, and 8.8 weight % Si_8O_{12} SC-POSS-Kapton[®].

Figure 5. Dynamic Mechanical Thermal Analysis of 0, 7, and 8.8 weight % Si_8O_{12} SC-POSS-Kapton[®] with final cure at 275 ˚C for 2 hours (0 % POSS, 7.0 % SC POSS, and 8.8 % SC POSS), and at 275 ˚C for an additional 16 hours (0 % POSS 275 ˚C, 7.0 % SC POSS 275 ˚C, and 8.8 % SC POSS 275 ˚C).

In our study, the films were solvent-cast by pouring the POSS poly(amic acid) onto a glass plate with no blade casting or forced directionality. As seen in Figures 6 and 7, the 7.0 and 8.8 wt % Si_8O_{11} MC-POSS-Kapton[®] films appear to have areas of good POSS dispersion and areas with darkened POSS-POSS aggregates, creating lamellae that are approximately 5 nm wide. There are also a very small number of darkened spheres approximately 5 nm wide. Fabrication of MC-POSS-Kaptons[®] has been carried out with much iteration over a multi-year time span, resulting in films with consistent physical properties and surface morphologies per MC-POSS content. Further investigation of these materials by Energy Dispersive X-ray Analysis (EDX) may clarify the composition of the darkened areas.

The SC-POSS-Kaptons[®] result in differing TEM images per weight % POSS. These newer materials are under analysis for characteristic morphologies. Despite the differences between MC- and SC-POSS-Kaptons[®], the physical properties are fairly similar. As shown in the following, the AO-resistance data is better correlated with weight % POSS than the position of the POSS comonomer, relative to the polymer chain.
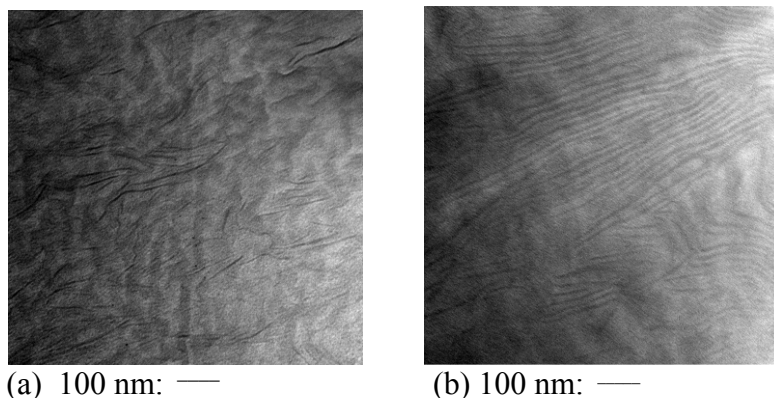

(a) 100 nm: ——   (b) 100 nm: ——

Figure 6. TEM image of 8.8 wt % Si_8O_{11} MC-POSS-Kapton[®] measured at (a) HV = 120 kV, Direct Magnification: 150000x, and (b) HV = 120 kV, Direct Magnification: 200000x.
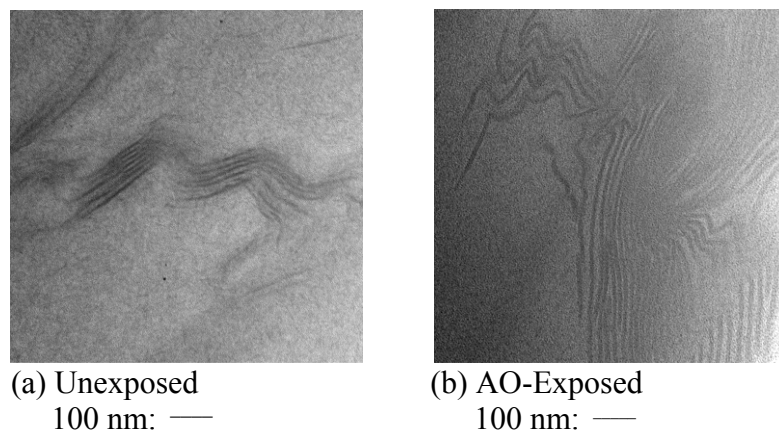

(a) Unexposed   (b) AO-Exposed
100 nm: ——   100 nm: ——

Figure 7. TEM image of 7.0 wt % Si_8O_{11} MC-POSS-Kapton[®] measured at (a) HV = 120 kV, Direct Magnification: 150000x, and (b) HV = 120 kV, Direct Magnification: 200000x.

The series of SC-POSS-Kaptons[®] was exposed to AO with a total fluence of 2.7 x 10^{20} O atoms cm^{-2}. Results, in Table 1, indicate dramatic decreases in surface erosion with increasing POSS content. In an AO exposure with a total fluence of 3.53 x 10^{20} O atoms cm^{-2}, 7 % Si_8O_{12} SC-POSS-Kapton[®] had an erosion yield that was 3.3 % of Kapton H[®]. In a separate AO exposure with a total fluence of 4.10 x 10^{20} O atoms cm^{-2}, 7 % Si_8O_{11} MC-POSS-Kapton[®] had an erosion yield that was 3.8 % of Kapton H[®]. These materials were also exposed side by side to 2.68 x10^{20} O atoms cm^{-2}. The % erosion of the POSS-Kaptons[®] relative to Kapton H[®] were 4.25 ± 0.48 microns for 7 wt% Si_8O_{11} MC-POSS-Kapton[®] and 4.86 ± 0.47 microns for 7 wt% Si_8O_{12} SC-POSS-Kapton[®]. The laboratory-scale synthesis of the polymer films is likely to produce slight differences in molecular weights and cure cycles, thus potentially having minor affects on the AO-erosion of the materials. The limited existing data indicates the effects of MC-POSS and SC-POSS on POSS-Kapton[®] film erosion are comparable.

MC-POSS-Kapton[®] films were flown on MISSE1 at about 500 km for 3.9 years. The samples were placed such that they experienced the RAM direction and therefore all aspects of LEO. Various images of the samples were taken throughout the flight which show that the 0 % POSS-Kapton[®] was completely eroded in less than four months. The innermost portion of the retrieved samples were thinner indicating they experienced greater erosion than the portion closer to the unexposed (masked) area, and/or they were thinner in this center area before flight. The step heights from the unexposed area and the neighboring exposed portion of the sample were measured in 12 places around the circumference of the exposed sample area. From these measurements, it was determined that the thickness of the masked 0 % POSS-Kapton[®] is 32.6 ± 0.9 µm. The erosion data is shown in Table 2, and SEM images of the flown 1.75 wt %, and 3.5 wt % Si_8O_{11} MC-POSS-Kaptons[®] are shown in Figures 8 and 9. It was determined by XPS that the atomic percentages of the top 10 nm of both POSS-Kapton[®] films were 34 % Si, 59 % O, and 7 % C for both the 1.75 and 3.5 wt% Si_8O_{11} MC-POSS-Kapton[®] samples.

Table 1. AO Erosion Data of SC-POSS-Kapton[®] Polyimides

Weight % Si_8O_{12} in SC-POSS-Kapton[®]	Kapton[®]-Equivalent Fluence / 10^{20} O atoms/cm^2	Erosion Depth (µm)	% Erosion of Kapton H[®] Witness Sample
1.75	2.71	1.99 ± 0.01	24.5
3.5	2.66	1.29 0.05	16.15
7.0	2.68	0.390 ± 0.04	4.9
8.8	2.68	0.132 ± 0.02	1.64
10.5	2.71	0.249 ± 0.03	3.06
12.3	2.71	0.113 ± 0.03	1.39
14.0	2.71	Undetectable	~ 0

Table 2. MISSE1 Flight MC-POSS Kapton[®] Erosion Data

Sample	[a]Average Step Height in microns	Standard Deviation in microns	Erosion in 3.9 years
0 wt % Si_8O_{11} MC-POSS Kapton[®]	32.6	0.9	[b]240
1.75 wt % Si_8O_{11} MC-POSS Kapton[®]	5.8	1.3	5.8
3.5 wt % Si_8O_{11} MC-POSS Kapton[®]	2.1	0.3	2.1

[a]Data from 12 step-height measurements around the perimeter of exposed area of circular sample with neighboring outer ring masked and not exposed to LEO.
[b]0 % POSS-PI total erosion estimated using AO fluence. Estimate for total flight is 8 x 10^{21} atoms/cm^2.
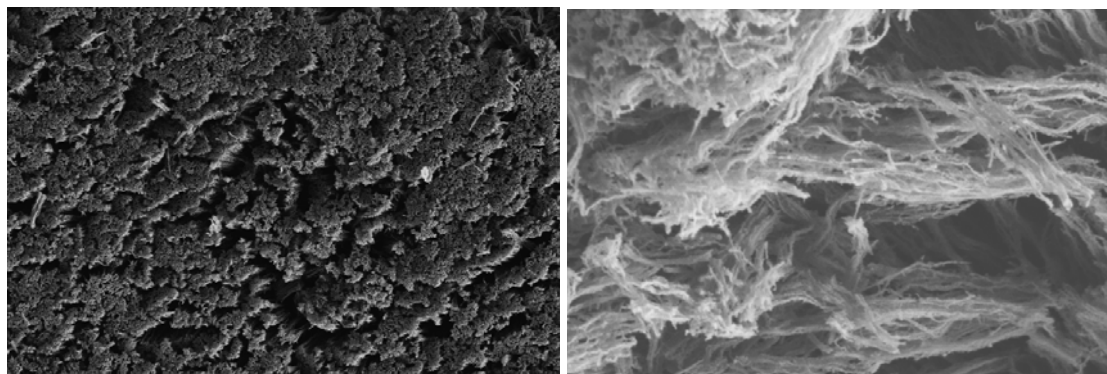
(a.) 10 microns = ——   (b.) 200 nm = —

Figure 8. Scanning Electron Micrographs of (a.) (b.) 1.75 wt % Si_8O_{11} MC-POSS-PI flown on MISSE1 and (c.) 3.5 wt % Si_8O_{11} MC-POSS-PI flown on MISSE1.
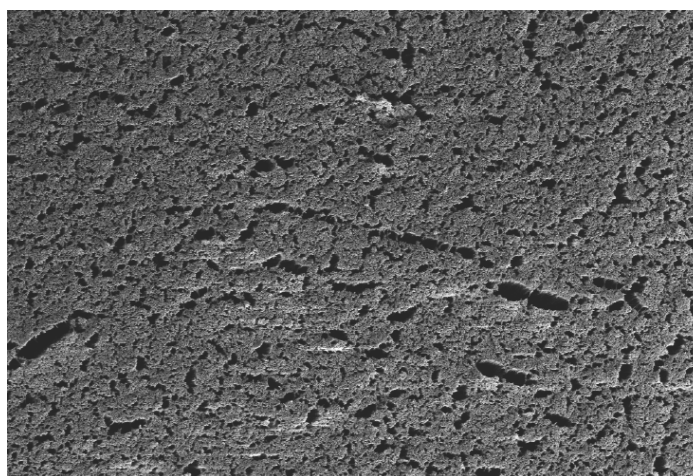

Figure 9. Scanning Electron Micrograph 3.5 wt % Si_8O_{11} MC-POSS-PI flown on MISSE1. 10 microns = ———

0, 1.75, 3.5, 5.25, and 7.0 wt % Si_8O_{11} MC-POSS-Kaptons[®] were flown on MISSE5 in LEO for about one year and experienced an approximate AO fluence of 1.8 x 10^{20} atoms cm^{-2}. Samples were located on the top side of the International Space Station and, although they were exposed to all aspects of LEO, they were situated such that a part of the ISS obstructed the RAM and so a much less harsh environment was experienced. All samples survived and erosion depths decreased with increasing POSS content as shown in Table 2. As is the case with AO exposures in simulated LEO experiments, the commercial Kapton H[®] eroded less than the 0 % POSS-Kapton[®], which was synthesized by the same technique as the POSS-Kaptons[®].

Table 3. MISSE5 Flight Sample Erosion Data

Sample	Erosion Depth (μm)
Kapton H	2.42 ± 0.47
0 wt % POSS Kapton	2.89 ± 0.59
1.75 wt % Si_8O_{11} MC-POSS Kapton	1.15 ± 0.21
3.5 wt % Si_8O_{11} MC-POSS Kapton	0.44 ± 0.19
5.3 wt % Si_8O_{11} MC-POSS Kapton	0.31 ± 0.18
7.0 wt % Si_8O_{11} MC-POSS Kapton	0.25 ± 0.11

MC-POSS-Kaptons[®] and SC-POSS-Kaptons[®] containing 3.5, 7.0, and 8.75 wt % POSS cage are currently loaded on MISSE6 sample trays and will be exposed to LEO on the ISS. The MISSE6 flight is scheduled to begin in March 2008.

Conclusion

MC- and SC-POSS-Kaptons[®] were found to have comparable AO-resistance in a simulated LEO environment, and similar physical properties. It was found that the incorporation of POSS slightly reduces the glass transition temperature (T_g) of Kapton[®], however, T_g values of POSS-Kaptons[®] are well above the temperatures experienced by materials in many applications. The modulus, T_g, and CTE of SC-POSS-Kaptons[®] were determined before and after exposure to atomic oxygen, and are comparable to the values of these properties for Kapton H[®]. The SC-POSS monomer is synthesized by facile methods, transparent flexible films can be prepared at higher SC-POSS loadings than MC-POSS, and a SC-POSS-Kapton[®] sheet has been industrially fabricated.

MC-POSS-Kapton[®] samples were flown in low Earth orbit for nearly four years on MISSE1 and for about one year on MISSE5. The 0 % POSS-Kapton[®] sample completely eroded within four months, while a thin film of the 3.5 wt % Si_8O_{11} POSS-Kapton[®] remained after flight, thereby demonstrating space-survivability. MC-POSS-Kaptons[®] were also flown on MISSE5 and again exhibited decreasing erosion in low Earth orbit with increasing POSS content.

Acknowledgment

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